

VOLTAMMETRIC STUDY AND ELECTROCHEMICAL DEGRADATION OF REACTIVE DYES

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Abstract

The aim of this study was, in a first stage, to investigate the voltammetric behavior of two reactive dyes, C.I.Reactive Orange 16 and C.I.Reactive Blue 19. Cyclic voltammetry technique (CV), on a glassy carbon electrode, was used for this purpose in order to identify the electrochemical activity of the chromophore group in each case, in the present experimental conditions. A second part of the study was to investigate the electrochemical degradation of the dyes, in the presence of hydrogen peroxide and copper ions. The reaction between the two species leads to the generation of hydroxyl radicals, which causes the oxidation and degradation of the organic compounds. The efficiency of dye degradation and decolorization were evaluated by color removal and COD values. Depending on electrolysis time, applied potential, hydrogen peroxide concentration and dye concentration, different stages of color removal were attained.

Key Words: Reactive dyes; cyclic voltammetry; electrochemical degradation; hydroxyl radical; copper ions

1. INTRODUCTION

Reactive dyes are the main group of dyes used in the textile industry. They contain one or more reactive groups capable of forming covalent bonds with a hydroxyl or amino group on the fiber. The strong covalent bond produced would be expected to give excellent wash fastness properties. However, the efficiency of the dye-fiber reaction varies from 50 to 90% (Guaratini et al., 2001), depending on the application method, depth of shade and dye type. For instance, in the particular case of the C.I.Reactive Blue 19, the relatively low fixation efficiency (75-80%) is due to the competition between the formation of the reactive form and the hydrolysis reaction (Pelegrini et al., 1999). Once dyeing is completed, the dyed material is washed off several times to remove unfixed and/or hydrolysed dye. As a result, a significant amount of these compounds is lost directly to wastewaters during processing operations and will enter into the environment.

This is the case of the two reactive dyes C.I.Reactive Orange 16 and C.I.Reactive Blue 19. The first compound is a vinylsulphone azo dye (Figure 1),

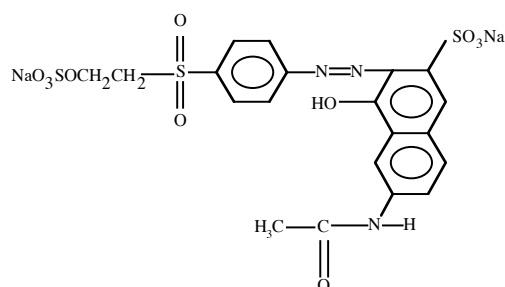


Figure 1 – Molecular structure of C.I. Reactive Orange 16

C.I. Reactive Blue 19 (Figure 2) is an anthraquinone-based vinylsulphone dye,

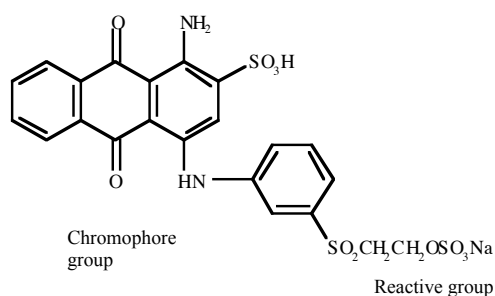


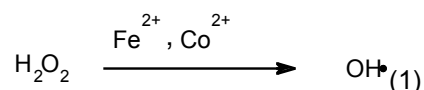
Figure 2 – Molecular structure of C.I. Reactive Blue 19

The presence of these dyes in wastewaters can be a considerable problem because of the potential for contamination of groundwater and drinking water supplies. So, detection, identification and degradation of reactive dyes are very important areas of study.

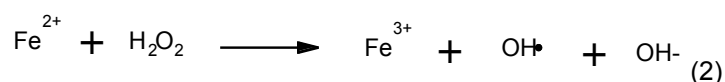
The aim of this study was, in a first approach, to investigate the voltammetric behavior of the two reactive dyes, using the cyclic voltammetry technique (CV) on a glassy carbon electrode. It is known that the electrochemical activity of the chromophore group can be identified in the case of the two reactive dyes. For C.I. Reactive Orange 16 dye, a voltammetric peak can be identified, caused by the irreversible reduction of the azo group, at a hanging mercury drop electrode (Zanoni et al., 1999). In the case of the C.I. Reactive Blue 19 dye, the reversible reduction process of the anthraquinone moiety can be followed by the CV technique at a hanging mercury drop electrode (Zanoni et al. 1999, Zanoni et al., 1997). In both situations it was tried to have similar results on the glassy carbon electrode.

In the second part of the work, an electrochemical degradation method was applied, in the presence of H_2O_2 and Cu^+ ions, as a development of a previous study in which the action of the electrogenerated Cl_2 was considered (Esteves, Dinis, 2004). The potential use of electrochemistry for the treatment of such wastewaters has been differentiated between electrochemical conversion of the contaminant to complete combustion of the organic materials or to a form to be degraded using other methods. Several electrochemical methods for degradation of dyes as been reported, like electrolysis process (Esteves, Dinis, 2004) or photocatalytic degradation electrochemically assisted (Pelegri et al., 1999). On the other hand, H_2O_2 is used, for a long time, in decolorization of dyeing wastewater, especially in the so called advanced oxidation processes (AOP), combined with UV radiation, ozone and Fenton's reagent (Kurbus et al., 2003), ultrasound (Voncina, Le Marechal, 2003) or with the electrochemical degradation in the presence of cobalt ions (Chen et al., 2003).

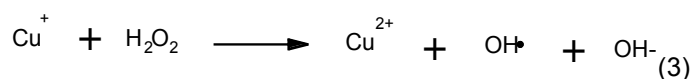
It is well known that strong oxidants like H_2O_2 or O_3 can degradate heterocyclic and aromatic molecular structures like dyes. This action is enhanced when other agents, like UV light or metals, are added to the degradation process. H_2O_2 itself requires high concentration and long contact time. However, activation by metals, like Fe or Co (Chen et al., 2003), can promote the catalytic decomposition of the oxidant agent, leading to the formation of strong radicals (Doré, 1989),



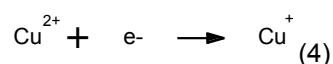
An example of this situation is Fenton's reagent,



In the present study, the catalytic action of Cu^+ ions must be,



This reaction is a source of hydroxyl radical production by chemical means and is entirely achieved by electrochemistry. To attain this, an initial quantity of Cu^{2+} ions is added to the solution, at the same time as H_2O_2 . The cathodic reaction



guarantees the radical production in order to achieve dye oxidation and degradation.

2. EXPERIMENTAL PROCEDURES

2.1 Solution and dyebath preparation

Dye solutions (10^{-3} M) for voltammetric analysis were prepared from the commercial products in the range pH 2-10 (buffered solutions).

Simulated dyebaths were prepared according the composition commonly used for cotton dyeing. C.I.Reactive Blue 19 and C.I.Reactive Orange 16 were included in concentration 3% (o.w.f.). Several auxiliary products were added to dyebath: Na_2CO_3 (5 gL^{-1}), NaOH 38°Bé (2 mL^{-1}), Na_2SO_4 (50 gL^{-1}). The analyzed solutions consisted on 5% and 20% of these initial dyebaths, simulating different textile wastewaters.

2.2 Cyclic voltammetry

Voltammetric measurements were carried out using a potentiostat HI-TEK DT 2101 and a galvanostat HI-TEK PPR1, controlled by electrochemical software, Picolog. The used cell in cyclic voltammetry experiments was an Amel three-electrode type. The working electrode was a Metrohm glassy carbon disc, of 0.3mm diameter, polished between experiments. An Ingold Pt auxiliary electrode and an Ingold saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Cyclic voltammograms were obtained with a scan rate of 20 mVs^{-1} , between 100 and -1000mV . Experiments were carried out at room temperature and in the presence of KCl as supporting electrolyte.

2.3 Electrochemical procedure

Electrolysis apparatus consisted of a 570 mL closed cell and two Ti/RuO₂ electrodes, 2 cm apart from each other and dipped into the solution. The total effective electrode surface area was 64 cm^2 . A power unit Farnell 30-10 controlled the power input. Potential values of 6 and 8 V were applied in controlled potential experiments. Two concentration values of H_2O_2 were tested, 15 and 4.5 mL^{-1} ; for hydrogen peroxide activation an initial solution of 0.12 mM Cu^{2+} was used (CuSO_4). COD and color measurements were made using standard methods. Experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1 Voltammetric study of C.I.Reactive Orange 16 and C.I.Reactive Blue 19

The voltammetric behavior of C.I.Reactive Orange 16 was studied in buffered solutions from pH 2 to 10. The irreversible reduction peak, assigned to the reduction of the azo group, should be identified in the range -350 to -650mV (Ag/AgCl), until pH 5 (Zanoni et al. 1999). However, even with an accumulation time of 90 s, it was not possible to obtain well-defined voltammograms in the considered experimental conditions. A cathodic wave was recognized nearby -500 mV (SCE) and at pH 2, but rather broad (Figure 3).

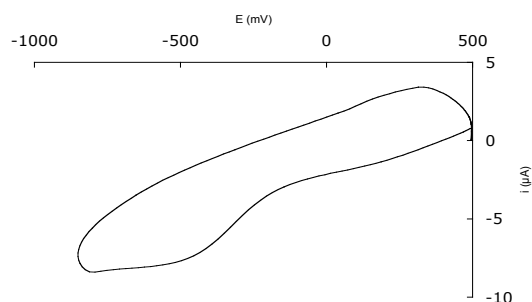


Figure 3 – Cyclic voltammogram of C.I. Reactive Orange 16, 10^{-3} M solution, pH 2 (first scan), glassy carbon electrode, SCE, scan rate 20 mVs^{-1}

In the case of C.I. Reactive Blue 19, the reduction of the anthraquinone group takes place by the mechanism of reversible quinone reduction to hydroquinone. In the pH interval 2 to 11 this reversible electrochemical reaction occurs in the potential range -200 to -650 mV vs Ag/AgCl (Zanoni et al., 1995). A reduction peak is observed nearby -450 mV (SCE) at pH 2, and the correspondent oxidation peak is suggested at -350 mV (SCE). The cyclic voltammogram shows the cathodic and anodic waves but, once more, not well-defined (Figure 4). As before, experiments with accumulation time gave no better results.

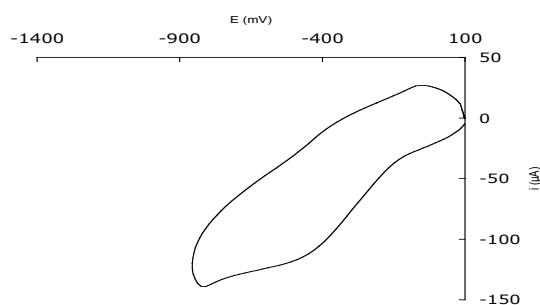


Figure 4 – Cyclic voltammogram of C.I. Reactive Blue 19, 10^{-3} M solution, pH 2 (first scan), glassy carbon electrode, SCE, scan rate 20 mVs^{-1}

CV results reveal the presence of reduction and oxidation peaks what can identified the electrochemical activity of chromophore group in both dyes. However, cyclic voltammograms were not sufficiently well-defined in order to allow a further investigation in the considered experimental conditions, for instance, to follow the discolouration process. Sometimes, such results are caused by chemical reactions coupled to the electrochemical reaction, too fast redox processes or solid electrode material.

3.2 Electrochemical degradation of C.I. Reactive Orange 16 and C.I. Reactive Blue 19

For dye degradation study two concentrations were considered, 5 and 20% of initial dyebath. Initial COD values and after 4 hours of electrochemical treatment, as well color removal, are presented in Tables 1 and 2 for C.I. Reactive Orange 16 and C.I. Reactive Blue 19, respectively.

Table 1 - C.I.Reactive Orange 16 – 4 hours of electrochemical treatment

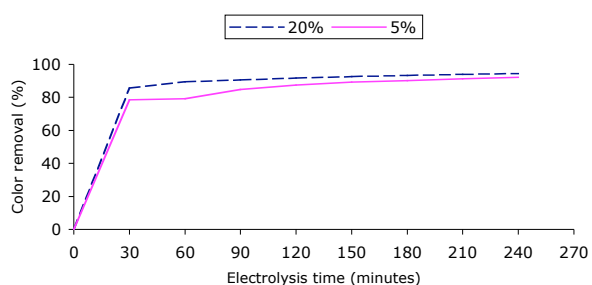
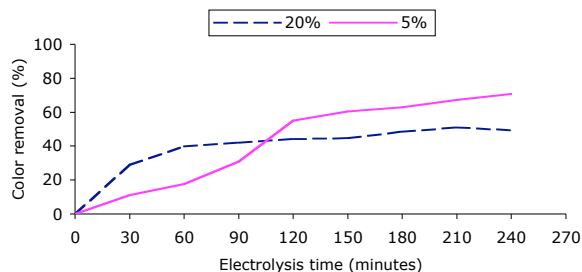
Solution (%)	H ₂ O ₂ (mL ⁻¹)	Cu ²⁺ (mM)	Applied potential (V)	COD (mg O ₂ L ⁻¹)		Color removal (%)
				Initial	Final	
5	4.5	0	6	90.0	57.9	19.0
	4.5	0.12	6	101.4	26.7	92.2
	4.5	0.12	8	101.4	31.6	93.4
	15	0.12	6	101.4	107.8	86.9
20	4.5	0.12	6	205.2	195.5	94.4
	4.5	0.12	8	205.2	135.4	95.6
	15	0.12	6	205.2	192.2	93.7

Table 2 - C.I.Reactive Blue 19 – 4 hours of electrochemical treatment

Solution (%)	H ₂ O ₂ (mL ⁻¹)	Cu ²⁺ (mM)	Applied potential (V)	COD (mg O ₂ L ⁻¹)		Color removal (%)
				Initial	Final	
5	4.5	0.12	6	68.9	145.2	68.6
	15	0.12	6	68.9	62.4	70.6
	15	0.12	8	68.9	51.04	71.8
20	4.5	0.12	6	273.4	240.9	30.3
	15	0.12	6	273.4	137.1	49.3
	15	0.12	8	273.4	166.3	20.3

The first result in Table 1 (C.I. Reactive Orange 16, 5% solution) shows that in absence of copper ions color removal is very low (19%), because activation of hydrogen peroxide does not occur. In the same experimental conditions but in the presence of copper ions color removal reaches 92.2%. On the other hand, it is easier to degrade the chromophore group of the azo dye (C.I. Reactive Orange 16) than the chromophore of the anthraquinone dye (C.I. Reactive Blue 19). This was a predictable result considering what can be observed with other treatment methods (Carneiro et al., 2004).

In the case of the C.I. Reactive Orange 16, a higher applied potential does not improve color removal in a significant way. This probably means that 6 V is enough to degrade this azo dye. In which concerns hydrogen peroxide concentration color removal results are better with the lowest value. However, the presence of this product can interfere in COD determination by possible reaction with the substances used in this analysis, such as potassium dichromate (VI). After electrochemical treatment all azo dye solutions in a 1:20 dilution were colorless. Considering color removal evolution during electrolysis procedure, an example is presented in Figure 5 for C.I.Reactive Orange 16, it is possible to conclude that a significant decrease in color is evident in the first stage of the process (more than 80% after 30 min), meaning that a considerable decolorization is possible with shorter electrolysis time.

**Figure 5** – Electrolysis at 6V of 5% and 20% solutions of C.I. Reactive Orange 16, in the presence of Cu²⁺ and 4.5 mL⁻¹ H₂O₂**Figure 6** – Electrolysis at 6V of 5% and 20% solutions of C.I. Reactive Blue 19, in the presence of Cu²⁺ and 15 mL⁻¹ H₂O₂

In the case of C.I. Reactive Blue 19 lower values of color removal were achieved as can be seen in Figure 6. In this case, a higher concentration of hydrogen peroxide leads to better results but it seems to be insufficient. In which concerns applied potential, electrolysis at 8 V gave a more significant color removal but only with 5% solutions. In the same experimental conditions, 20% solutions present a color removal of 20.3%. A possible explanation can be an insufficient concentration of hydrogen peroxide and copper ions to promote anthraquinone dye degradation and an effective decolorization of solutions.

Considering COD removal, in all situations lower values are obtained after treatment, with two exceptions likely caused by hydrogen peroxide reaction presence.

4. CONCLUSION

Voltammetric techniques such as cyclic voltammetry are a suitable way to follow reactive dyes behaviour during electrochemical degradation, by the disappearance of the characteristic intensity peaks in the voltammograms. In the present case experimental conditions did not allow clear results in order to progress in voltammetric investigation. This point must be reconsidered in further studies.

Electrochemical procedure is an important alternative approach for textile wastewater treatment. Particularly electrochemical oxidation by radicals action, initiated by hydrogen peroxide activation in the presence of copper ions, seems to have an effective result in the case of reactive azo dyes. Anthraquinone dyes are more difficult to decompose by this way, probably needing a higher concentration of hydroxyl radicals in order to achieve complete oxidation and degradation of the dye. In both cases, an acceptable solution must consider electrochemical processes as part of a more complete plan of textile wastewater treatment in addition to other techniques, permitting a significant reduction in electrolysis time.

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